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A REVIEW OF LABORATORY TESTS ON THE TOXICITY OF SOME N-SUBSTITUTED p-BROMOBENZENESULFONAMIDES TO VARIOUS ARTHROPODS

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Twenty-one N-substituted p-bromobenzenesulfonamides have been prepared and tested against 21 species of arthropods, and some have shown appreciable insecticidal activity. The results of these tests, which were conducted by various entomologists and former entomologists of this Division including E. C. Cushing, J. B. Gahan, W. A. Gersdorff, E. L. Mayer, E. R. McGovran, R. Melvin, N. Mitlin, P. G. Piquett, D. D. Questel, E. H. Siegler, M. C. Swingle, and A. P. Yerington, are given below. Some of the tests have been reported previously.

Preparation

The compounds were prepared by reacting p-bromobenzenesulfonyl chloride with the appropriate amine or amino compound under suitable conditions. Most of them are colorless solids. These sulfonamides are listed in table 1 with index numbers, under which the entomological data are given in table 2.

Test Methods

The usual test procedures were followed and are described only briefly below or references are given. Compounds were finely ground and applied in suspension or solution as a spray or in a dust. Where exposure time is not mentioned, it will be found either in the reference cited or in the test results.

American cockroach (Periplaneta americana (L.)).--Three-fourths-grown nymphs were dusted in a battery jar with 0.25 gram of the compound and confined for 3 days.

Cabbage looper (Trichloplusia ni (Hbn.)).--Third instars were fed dusted or sprayed collard leaves.

Codling moth (Carpocapsa pomonella (L.)).--Tests were conducted by the apple-plug method (5) on newly hatched larvae infested shortly after application. Each compound was sprayed at 4 pounds per 100 gallons.

Colorado potato beetle (Evergestis rimosalis (Guen.)).--Fourth instars were fed dusted collard leaves for 2 days or exposed on collard leaves in fumigation tests for 1 day.

Cross-striped cabbageworm (Leptinotarsa decemlineata (Say)).--Fourth or fifth instars were fed treated collard leaves (1).

European corn borer (Pyrausta nubilalis (Hbn.)).--Newly hatched larvae were fed sprayed cauliflower leaves and the kill was determined after 48 hours.

Hawaiian beet webworm (Hymenia recurvalis (F.) = fascialis (Gram.)).--Fourth instars were fed dusted or sprayed pigweed, except for p-bromobenzenesulfonamide (No. 1), which was dusted on Swiss chard and fed to fifth instars (1).

House fly (Musca domestica L.).--The tests were made by the turntable method (3). Two solutions were compared to show whether a compound had any synergism; one solution contained the compound alone dissolved in deodorized kerosene containing 10 percent of acetone and the other also contained 0.5 mg. of pyrethrins per milliliter. The standard pyrethrum solution containing 0.5 mg. of pyrethrins gave 8-17 percent kill. All compounds were tested at 1-percent concentration or in a saturated solution where solubility was less than 1 percent.

Imported cabbage worm (Pieris rapae (L.)).--Third instars were fed sprayed collard leaves for 6 days.

Large milkweed bug (Oncopeltus fasciatus (Dall.)).--Adults were dusted directly and fed untreated milkweed seeds for 3 days (1).

Melonworm (Diaphania hyalinata (L.)).--Fourth or fifth instars were fed dusted or sprayed pumpkin or squash leaves for 2 to 4 days.

Mexican bean beetle (Epilachna varivestis Muls.).--Fourth instars were exposed on leaves sprayed with a 1-percent solution to give a deposit of 16 to 18 micrograms per square centimeter (4).

Pseudoplusia looper (Pseudoplusia rugationis (Guen.)).--Fourth instars were fed dusted or sprayed collard leaves for 3 to 6 days.

Pickleworm (Diaphania nitidalis (Stoll)).--Fourth instars were fed dusted or sprayed pumpkin leaves (1).

Red spider mite (Tetranychus telarius (L.)).--Adults and nymphs were fed dusted castor bean or snap bean leaves and exposed for 3 days.

Screw-worm (Callitroga hominivorax (Cqrl.)).--The jar method (2) was used on newly hatched larvae.

Southern armyworm (Prodenia eridania (Cram.)).--Various instars were fed dusted or sprayed collard, pigweed, or Swiss chard (1). A few fumigation tests were made.

Southern beet webworm (Pachyzancla bipunctalis (F.)).--Fourth or fifth instars were fed dusted or sprayed Swiss chard (1).

Squash bug (Anasa tristis (DeG.)).--Nymphs were fed dusted pumpkin stems (1).

Three-striped blister beetle (Epicauta lemniscata (F.)).--Adults were fed dusted or sprayed pigweed or Swiss chard (1).

Results

A compound was considered toxic to screw-worms if the minimum lethal concentration was not over 0.1 percent. In the codling moth tests, compounds giving less than 50 percent of wormy fruit were considered toxic. For all the other species a 75-percent kill was the criterion of toxicity. On this basis the following compounds were found to be toxic to one or more species of arthropods. Numbers preceding names are the same as index numbers in table 1 and are included to facilitate comparison of compounds.

(2)	p-bromo-N-ethylbenzenesulfonamide	10 species
(3)	p-bromo-N-propylbenzenesulfonamide	10
(1)	p-bromobenzenesulfonamide	8
(7)	p-bromo-N,N-dimethylbenzenesulfonamide	7
(5)	p-bromo-N-isobutylbenzenesulfonamide	5
(12)	4-bromo-2'-chlorobenzenesulfonanilide	3
(14)	4-bromo-4'-chlorobenzenesulfonanilide	3
(17)	4-bromobenzenesulfonanisidide	1
(20)	p-bromophenylsulfonylmorpholine	1
(4)	p-bromo-N-butylbenzenesulfonamide	1

Test results for these compounds are shown in table 2 with the following exceptions. None of the compounds tested met the criteria for toxicity to the Mexican bean beetle, house fly, or squash bug; these insects therefore are not listed in the table. Furthermore, a few insect species were subjected to tests with only one or two compounds. The results of these tests are given below:

Cabbage looper.--Compound No. 3 at 8 lb./100 gal. gave 100-percent kill after 6 days; No. 12 at 140 µg./sq. cm. gave 44-percent kill after 3 days.

Imported cabbage worm.--Compound No. 3 at 8 lb./100 gal. gave 100-percent kill.

Large milkweed bug.--No. 7 at 230 µg./sq. cm. gave 17-percent kill, and No. 14 at 355 µg./sq. cm. gave 4-percent kill.

Pseudoplusia looper.--No. 14 at 420 µg./sq. cm. gave 72-percent kill, and No. 12 at 8 lb./100 gal. gave 70-percent kill.

Pickleworm.--No. 7 at 370 µg./sq. cm. or at 2 lb./100 gal. gave 100-percent kill.

It is significant that of the 21 compounds tested 10 were toxic to at least one insect species. Since very few of the compounds were tested against all the species, further tests might have shown toxicity to other insects. It is worthy of note that the most toxic compounds of the group included bromobenzenesulfonamide itself and the lower aliphatic N-substituted amides. The aromatic and heterocyclic compounds in general showed much less toxicity.

p-Bromo-N-ethylbenzenesulfonamide and p-bromo-N-pentylbenzenesulfonamide were also weak synergists for pyrethrum when used against the house fly.

Literature Cited

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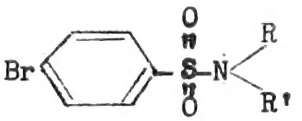
Table 1.--p-Bromobenzenesulfonamides tested against 21 species of arthropods.



No.	Compound	R	R'	Empirical formula	Melting point (°C.)
1	Benzenesulfonamide, p-bromo-	H	H	$C_6H_6BrNO_2S$	166-7
2	p-bromo-N-ethyl-	H	C_2H_5	$C_8H_{10}BrNO_2S$	81-2
3	p-bromo-N-propyl-	H	C_3H_7	$C_9H_{12}BrNO_2S$	66.5-7.5
4	p-bromo-N-butyl-	H	C_4H_9	$C_{10}H_{14}BrNO_2S$	56
5	p-bromo-N-isobutyl-	H	$CH_2CH(CH_3)_2$	$C_{10}H_{14}BrNO_2S$	100.5-1.5
6	p-bromo-N-pentyl-	H	C_5H_{11}	$C_{11}H_{16}Br\ NO_2S$	58.5-9.5
7	p-bromo-N,N-dimethyl-	CH_3	CH_3	$C_8H_{10}BrNO_2S$	93-4
8	p-bromo-N,N-diethyl-	C_2H_5	C_2H_5	$C_{10}H_{14}BrNO_2S$	--
9	N-benzyl-p-bromo-	H	$CH_2C_6H_5$	$C_{13}H_{12}BrNO_2S$	120-30
10	N,N-dibenzyl-p-bromo-	$CH_2C_6H_5$	$CH_2C_6H_5$	$C_{20}H_{18}BrNO_2S$	--
11	p-bromo-N-(1-naphthyl)-	H	$C_{10}H_7$	$C_{16}H_{12}BrNO_2S$	--
12	Benzenesulfonanilide, 4-bromo-2'-chloro-	H	C_6H_4Cl	$C_{12}H_9BrClNO_2S$	105.5-6.5
13	4-bromo-3'-chloro-	H	C_6H_4Cl	$C_{12}H_9BrClNO_2S$	93-103
14	4-bromo-4'-chloro-	H	C_6H_4Cl	$C_{12}H_9BrClNO_2S$	135-6

Table 1.--Continued

No.	Compound	R	R'	Empirical formula	Melting point (°C.)
15	Benzenesulfonanilide, 4-bromo-N-methyl-	CH_3	C_6H_5	$C_{13}H_{12}BrNO_2S$	--
16	4,4'-dibromo-	H	$C_6H_4Br(4)$	$C_{12}H_9Br_2NO_2S$	142
17	p-Benzenesulfonanisidide, 4-bromo-	H	$C_6H_4OCH_3$	$C_{13}H_{12}BrNO_3S$	145-6
18	o-Benzenesulfonotoluidide, 4-bromo-	H	$C_6H_4CH_3$	$C_{13}H_{12}BrNO_2S$	115.5-17.5
19	p-Benzenesulfonotoluidide, 4-bromo-	H	$C_6H_4CH_3$	$C_{13}H_{12}BrNO_2S$	100-100.5
20	Morpholine, N-(p-bromophenylsulfonyl)-	--	$-(CH_2)_2O(CH_2)_2-$	$C_{10}H_{12}BrNO_3S$	--
21	Piperidine, N-(p-bromophenylsulfonyl)-	--	$-(CH_2)_5-$	$C_{11}H_{14}BrNO_2S$	89-90

Table 2.--Toxicity of N-substituted p-bromobenzenesulfonamides to 12 insects[1,2/]

Compound No.	American cockroach	Codling moth		Colorado potato beetle		Cross-striped cabbageworm		European corn borer		Hawaiian beet webworm		Melonworm		Red spider mite		Screw-worm	Southern armyworm		Southern beet webworm		Three-striped blister beetle	
	Percent kill	Percent wormy	Percent stung	Application	Percent kill	Application	Percent kill	Application	Percent kill	Application	Percent kill	Application	Percent kill	Application	Percent kill	Minimum lethal concn. (percent)[3/]	Application	Percent kill	Application	Percent kill	Application	Percent kill
1	8	45	13	255	97	—	—	(2)	100	(8)	100	(8)	96	265	48	0.025	146	78	410	93	(8)	12
	—	—	—	F[4/]	0	—	—	—	—	355	100	(8)	90	—	—	—	(8)	54	(8)	100	310	96
	—	—	—	—	—	—	—	—	—	—	—	320	25	—	—	—	250	10	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	115	0	—	—	—	—
2	90	9	3	—	—	225	12	(4)	100	(8)	100	250	92	310	98	(eggs) 0.025-0.05	(8)	100	510	100	(4)	37
	—	—	—	—	—	(8)	41	—	—	—	—	(8)	100	265	76	—	510	100	(8)	100	215	100
	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(8)	100	—	—	—	—
3	100	83	2	—	—	270	0	(4)	97	—	—	125	72	310	33	0.05-0.10	300	76	300	81	(4)	12
	—	—	—	—	—	(8)	87	—	—	—	—	(4)	100	—	—	—	(8)	87	—	—	260	96
	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(8)	100	—	—	—	—
4	0	81	0	—	—	—	—	—	—	—	—	125	25	—	—	ST	250	25	250	78	155	24
5	0	81	1	—	—	(8)	33	(4)	82	220	20	230	68	200	25	NT	250	79	250	100	(4)	4
	—	—	—	—	—	—	—	—	—	(8)	100	(4)	100	—	—	—	(8)	90	(8)	100	185	36
	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	F[4/]	0	—	—	—	—
7	—	24	53	—	—	—	—	(8)	100	—	—	370	100	—	—	0.025-0.05	(8)	100	—	—	140	96
	—	—	—	—	—	—	—	—	—	—	—	(2)	100	—	—	—	370	100	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	F[4/]	0	—	—	—	—
12	0	92	0	—	—	—	—	(4)	19	(8)	9	170	76	—	—	NT	160	86	—	—	(8)	0
	—	—	—	—	—	—	—	—	—	240	96	—	—	—	—	—	(8)	100	—	—	160	0
14	0	74	4	—	—	—	—	(4)	0	(8)	96	(8)	96	—	—	NT	F[4/]	0	—	—	240	4
	—	—	—	—	—	—	—	—	—	185	88	260	80	—	—	—	240	100	—	—	(8)	32
17	—	99	0	—	—	240	36	(4)	19	—	—	260	64	—	—	NT	—	—	—	—	—	—
20	—	97	0	F[4/]	0	155	0	—	—	—	—	—	—	—	—	NT	170	0	—	—	—	—
	—	—	—	170	97	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

1/ For toxicity to other insects see text.

2/ Relative to application, numbers in parenthesis refer to sprays applied at given lbs./100 gal. Leaves were sprayed on both sides until thoroughly wet, then allowed to dry before the insects were placed on them. Other figures refer to dust applications expressed as micrograms per square centimeter.

3/ NT = nontoxic, ST = slightly toxic at 0.67 percent.

4/ Fumigant test in which insects were exposed to vapors from 0.3 g. of compound in a closed petri dish.